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FROM: PROI (TI) (STINFO)

03 October 2000

SUBJECT: Authorization for Release of Technical Information, Control Number: **AFRL-PR-ED-AB-2000-188**  
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**HEDM Contractors Conference (Park City, UT, 24 Oct 2000)**  
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# THEORY AND SYNTHESIS OF NEW HIGH ENERGY DENSITY MATERIALS

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The aim of this AFOSR program is the synthesis of novel HEDM compounds, exploiting the synergism between theory and synthesis. Theoretical calculations are routinely used to guide the synthesis efforts and to facilitate the identification and characterization of the products.

Under DARPA sponsorship, the synthesis of novel polynitrogen compounds was pursued. Last year, the successful synthesis of  $N_5^+AsF_6^-$  had been reported. The  $N_5^+$  cation is only the third known, homoleptic polynitrogen species that can be prepared and isolated in bulk, the other two being  $N_2$  and the azide anion.  $N_5^+AsF_6^-$  was only marginally stable and can explode. The  $N_5^+$  cation has now been successfully tamed by preparing the stable fluoroantimonate salts,  $N_5^+SbF_6^-$  and  $N_5^+Sb_2F_{11}^-$ . The former is stable up to 70 °C and, according to drop weight tests, is essentially insensitive. The crystal structure of  $N_5^+Sb_2F_{11}^-$  was determined, and the geometry of  $N_5^+$  was found to be in excellent agreement with that predicted by our theoretical calculations. A considerable amount of effort was spent on improving the syntheses of the precursors for  $N_5^+$  salts. This work resulted in the discovery of a new *cis-trans* isomerization process for  $N_2F_2$  and a disproportionation reaction of  $N_2F_2$  to give  $NF_4^+Sb_3F_{16}^-$  under mild conditions. Metathetical reactions were carried out between  $N_5^+SbF_6^-$  and alkali metal azides in pursuit of  $N_8$ . Furthermore, reactions of  $N_2F_3^+$  and  $N_2F_2$  with  $HN_3$  were studied. Attempts were made to find a easily accessible replacement for  $N_2F^+$  in its reactions with  $HN_3$  to give  $N_5^+$ . To this end, the protonation of  $N_2O$  was studied with  $N_2OH^+$  being the desired product, but all reactions were unsuccessful.

Efforts to prepare the  $N_{11}^+$  cation by the reaction of  $N_2F_3^+$  with 3 moles of  $HN_3$  were unsuccessful. The  $N_2F_3^+$  cation was initially reduced by  $HN_3$  to  $N_2F^+$  which then proceeded to react with  $HN_3$  to give  $N_5^+$ .

While carrying out structural studies of the  $NF_2O^+$  cation, which is another potential precursor for polynitrogen compounds, a new method for solving oxygen/fluorine positionally disordered crystal structures was discovered. This method was also successfully demonstrated for the  $SO_2F^-$  anion. In both cases, it was shown that the crystal structures obtained from disordered data sets with our method were in excellent agreement with those predicted by the theoretical calculations for the free gaseous ions.

In pursuit of novel powerful oxidizers that might be stronger than any presently known oxidizer, the following new concept was developed and tested. Cations are stronger oxidizers than their neutral parent molecules, which in turn are stronger oxidizers than their anions. Therefore, transition metal fluoride anions were prepared in their highest oxidation states by high temperature / high pressure fluorinations with elemental fluorine and then converted to the corresponding cations by acidification with strong Lewis acids. The resulting, thermally unstable cations are indeed very powerful oxidizers. This was successfully demonstrated for the  $NiF_3^+$  system, which was shown to be capable of oxidizing  $ClF_3$  and  $BrF_5$  to  $ClF_6^+$  and  $BrF_6^+$ , respectively. However, attempts to use this system for the preparation of the new  $OF_3^+$  or  $XeF_7^+$  cations were not successful. In a quest for finding the strongest possible oxidizer, the oxidizing strength of numerous transition metal fluoride cations that can be prepared in this manner, are presently being calculated by ab initio methods in collaboration with Dave Dixon. In connection with this work, the crystal structures of  $ClF_6^+$ ,  $BrF_6^+$ , and  $IF_6^+$  were determined in collaboration with McMaster University and their force fields were calculated by ab initio methods.

The study of the  $ClF_4^+$  cation, which was started last year, was completed, and extensive theoretical modeling of the influence of strong intermolecular fluorine bridging on the structure and the vibrational spectra was carried out. A simple method for simulating infinite chains by capping with HF was devised and shown to give excellent results. Results from a theoretical study of the closely related  $BrF_4^+$  and  $IF_4^+$  cations strongly disagreed with the previously

reported crystal structures and prompted their reinvestigation. It was shown that the previously reported structures were indeed in error and that the correct structures are in excellent agreement with the theoretical predictions. In the case of  $\text{IF}_4^+\text{SbF}_6^-$  a very interesting 9-coordinated environment was found for  $\text{IF}_4^+$ . In collaboration with Arkady Ellern, the crystal structure of solid  $\text{ClF}_3\text{O}$  was also determined and shown to consist of unusual tetrameric units.

Attempts to prepare and characterize the yet unknown  $\text{PO}_2^+$  cation, the analogue to the well-known  $\text{NO}_2^+$  cation, resulted in a surprise. Acidification of  $\text{PO}_2\text{F}_2^-$  salts with  $\text{SbF}_5$  did not produce the expected  $\text{PO}_2^+\text{SbF}_6^-$  but a tetrameric ring structure with P-O-Sb bridges and terminal P-F bonds. Similarly, attempts to prepare the novel  $\text{LiF}_2^-$  anion in the form of its  $\text{Cs}^+$  salt gave an unexpected highly bridged crystal structure with the correct composition but tetra-coordinated Li and octa-coordinated Cs.